Chapter 3

Catalytic activity of TPA/MCM-41 & TSA/MCM-41

- Esterification

(a) Esterification of dicarboxylic acids (Succinic acid & Malonic acid)

(b) Esterification of fatty acid (Lauric acid with butanol)

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RESEARCH LETTER

An efficient green catalyst comprising 12-tungstophosphoric acid and MCM-41: synthesis characterization and diesterification of succinic acid, a potential bio-platform molecule

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An efficient green catalyst comprising 12-tungstophosphoric acid (TPA) and MCM-41 was synthesized. The catalytic activity was evaluated for liquid phase solvent free diesterification of succinic acid. The support and the synthesized catalyst were characterized by various physico-chemical techniques. Fourier transform infrared, diffuse reflectance spectroscopy, and ^{31}P NMR spectra indicate that the Keggin structure of TPA was not destroyed after anchoring to MCM-41. X-ray diffraction, scanning electron microscopy, and transmission electron microscopy show that TPA is uniformly dispersed inside the channels without disturbing the hexagonal array of MCM-41. The present contribution reports solvent free diesterification of succinic acid with alcohols under mild reaction conditions. The catalyst shows higher activity toward diester, especially for dioctyl succinate 99% yield was obtained with very high turnover number, 12.43×10^4. Also the catalyst shows potential of being used as recyclable catalytic material after simple regeneration without loss of any catalytic activity.

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Synthesis and Characterization of 12-Tungstosilicic Acid Anchored to MCM-41 as well as Its Use as Environmentally Benign Catalyst for Synthesis of Succinate and Malonate Diesters

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ABSTRACT: 12-Tungstosilisic acid anchored to MCM-41 was synthesized and characterized by various physicochemical techniques such as thermogravimetric analysis (TGA), Fourier transform infrared (FT-IR), laser-Raman spectroscopy, diffuse reflectance spectroscopy (DRS), N_2 adsorption−desorption, ^{29}Si-magic-angle spinning (MAS) NMR, X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The total acidity was determined by *n*-butyl amine titration. The types of acidic sites (acidic strength) were determined by potentiometric titration. The use of synthesized material was explored for esterification of diacarboxylic acids with butanol. Influence of various reaction parameters (catalyst concentration, acid/alcohol molar ratio and reaction time) on catalytic performance was studied. The catalyst shows high activity in terms of higher yields toward diesters, especially for dioctyl succinate and dioctyl malonate. The catalyst was also regenerated and reused for four cycles. All these characteristics imply the high potential of an environmentally benign catalyst for synthesis of succinate and malonate diesters.

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Esterification of lauric acid with butanol-1 over $H_3PW_{12}O_{40}$ supported on MCM-41

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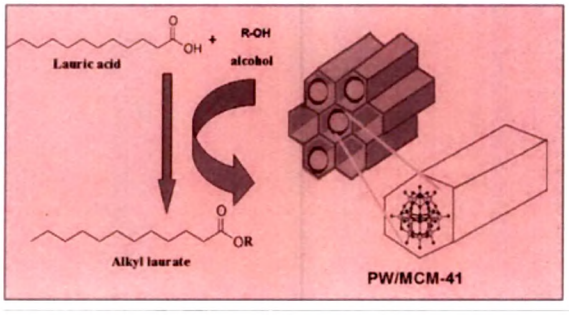
HIGHLIGHTS

- 12-tungstophosphoric acid anchored to MCM-41 was synthesized and characterized.
- Catalytic activity for esterification of lauric acid with n-butanol.
- Catalyst was recovered and reused up to four cycles.
- Esterification of lauric acid follows second order rate law.
- Activation energy was found to be 78 kJ mol^{-1}.

GRAPHICAL ABSTRACT



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ABSTRACT

Heterogeneous acid catalyst comprising 12-tungstophosphoric acid and MCM-41 was synthesized and characterized by surface area measurement (BET method), X-ray diffraction (XRD) and solid state ^{31}P MAS–NMR. The catalytic activity was evaluated for esterification of fatty acid, lauric acid with 1-butanol. Influence of various reaction parameters such as catalyst concentration, acid/alcohol molar ratio and reaction time were studied to optimize the conditions for maximum yields. Also the catalyst was recovered and reused up to four cycles. A study on the kinetic behavior was carried out by classical method and it was found that esterification of lauric acid follows second order rate law. The influence of temperature on rate constant was also studied and the activation energy was found to be 78 kJ mol^{-1}.

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(a) Esterification of dicarboxylic acids

The green chemical transformations of the bio-platform molecules can build up new environmentally compatible and sustainable chemical technologies. The biomass-derived platform molecules are potentially useful building blocks for chemical synthesis [1-3]. Among the top bio-platform molecules, recently succinic and malonic acid are gaining much importance as it can be converted to variety of products.

Esterification of diacarboxylic acids is very important as the obtained diesters are known to be entirely bio-renewable or green chemicals that can replace petroleum-based solvents. Due to their high oxygen content, many diesters are used as additives in Fuels. They are important intermediates in the synthesis of fine chemicals, drugs, plasticizers, food preservatives, pharmaceuticals and cosmetics. Among all, esters of succinic acid and malonic acid are most important as they find applications in synthesis of plasticizers, perfumes, fragrance in food and cosmetics, diluents in paints and coatings and intermediates in drugs, dye stuffs [4].

The conventional procedures for production of diesters involve a stirred batch or continuous reactor with sulphuric acid as a homogeneous catalyst. Due to the known disadvantages of traditional liquid acids, much attention has been paid to the development of ecologically and environmentally benign processes, by use of solid acid catalysts. A number of solid acid catalysts such as Clays [5-8], ion exchange resins [9], carbonaceous materials [10,11] and phosphotungstic acid anchored to Al-MCM-41 [12] have been reported for esterification of succinic acid. Most of the reported esterification of succinic acid have been carried out using solvents and at longer reaction period. A literature survey also shows that malonate esters have been generally synthesized by transesterification [13-15]. Transesterification of malonate esters requires high reaction temperature and time.

D. J. Miller and co-workers have reported esterification of succinic acid with ethanol catalyzed by macroporous Amberlyst-15 ion-exchange resin. The kinetic model was also proposed for the design and simulation of processes such as reactive distillation for diethyl succinate formation [9]. James H. Clark and co-workers reported mesoporous carbonaceous materials such Starbons, DARCO and NORIT with diversity of surface functional groups for esterification of succinic acid with ethanol [10]. They have also reported the application of tuneable carbonaceous materials prepared from carbonisation of expanded starch (Starbon) in esterification of succinic acid [11]. Y. Mansoori and F. S. Tataroglu reported esterification of mono- and dicarboxylic acids by tributyl borate under solvent- and catalyst-free conditions. There was no data about catalyst regeneration and recycling [16].

B.M. Choudary and his group has reported the use Fe^{3+}-montmorillonite clay catalyst for the first time to esterify various aliphatic, aromatic, α, β-unsaturated mono- and di-carboxylic acids and long chain fatty acids with alcohols [6]. B. S. Jai Prakash and his group reported esterification of dicarboxylic acids such as succinic acid, malonic acid, adipic acid and phthalic acid with various alcohols and phenols in presence of metal exchanged montmorillonite clay catalyst. Among the catalysts used, Al^{3+} exchanged montmorillonite clay was found to be the most effective catalyst **[5].** The same group has also reported a method for surface acidity study of M^{n+}-montmorillonite clay catalysts by FT-IR spectroscopy and its correlation with esterification activity **[7].** They have also reported activated Indian Bentonite for esterification of carboxylic acids with phenols and alcohols **[8].** U. Chudasama and co-workers reported synthesis of mono and diesters using a solid acid catalyst comprising zirconium titanium phosphate considerably at high temperatures and time [17]. V. Ramaswamy's group reported tin oxide-modified mesoporous SBA-15 molecular sieves catalyst and its activity in transesterification of a diketo ester such as diethyl malonate in the

presence of a number of alcohols to give both trans mono as well as diketo esters [18].

A literature survey shows that very few reports are available on esterification of dicarboxylic acids over HPAs anchored to mesoporous silica.

V. Murugesan and co-workers reported catalytic activity of Al-MCM-41 supported 12-tungstophosphoricacid in the esterification of succinic anhydride with ethanol for synthesis of mono and diesters [12]. At the same time, even though 12-tungstosilicic acid is the next acidic and stable [19-22] heteropoly acid in the Keggin series, not much work has been carried out for the same. T. Dogu et al have reported silicotungstic acid impregnated MCM-41 like mesoporous solid acid catalysts for dehydration of ethanol [23]. Halligudi et al reported silicotungstic acid/zirconia immobilized on SBA-15 for esterification [24]. Thus a literature survey shows that there are no reports for the use 12-tungstosilicicacid anchored to MCM-41 for esterification of dicarboxylic acids.

From the view point of environment as well as importance of succinate and malonate esters, the development of solvent free catalytic reaction would be of much interest in the area of green synthesis. Hence, keeping in mind the importance of green synthesis of succinate and malonate esters as well as anchored HPAs, in the present chapter we have made an attempt to develop green catalysts, TPA/TSA anchored to MCM-41 for esterification of dicarboxylic acids.

In the present chapter deals with solvent free esterification of succinic acid and malonic acid over green catalysts comprising TPA/TSA and MCM-41. Influence of various reaction parameters (catalyst concentration, acid/ alcohol molar ratio and reaction time) on catalytic performance was studied to optimize the conditions for obtaining maximum yields for diesters.

Esterification of succinic acid and malonic with different alcohols (Ethanol, hexanol, octanol) was also carried out under optimized conditions. The catalyst was regenerated and reused up to four cycles. Based on the catalytic results the best catalyst was also proposed.

Experimental

Materials

All chemicals used were of A.R. grade. Succinic acid, malonic acid n-butanol, hexanol and octanol were used as received from Merck.

Esterification of dicarboxylic acids.

The esterification reaction of malonic acid with alcohols was carried out in a 100 ml batch reactor provided with a double walled air condenser, Dean-Stark apparatus, magnetic stirrer and a guard tube. Dean-Stark apparatus was attached to a round bottom flask to separate the water formed during the reaction. The reaction mixture was refluxed at 80 °C for 4 h. The obtained products were analyzed on a Gas Chromatograph (Nucon-5700) using BP1 capillary column. Products were identified by comparison with the authentic samples and finally by Gas Chromatography-Mass Spectroscopy (GC-MS).

Results and Discussion

Esterification of dicarboxylic acids to diesters (figure 41) requires strong Bronsted acidity as compared to simple esterification reactions.

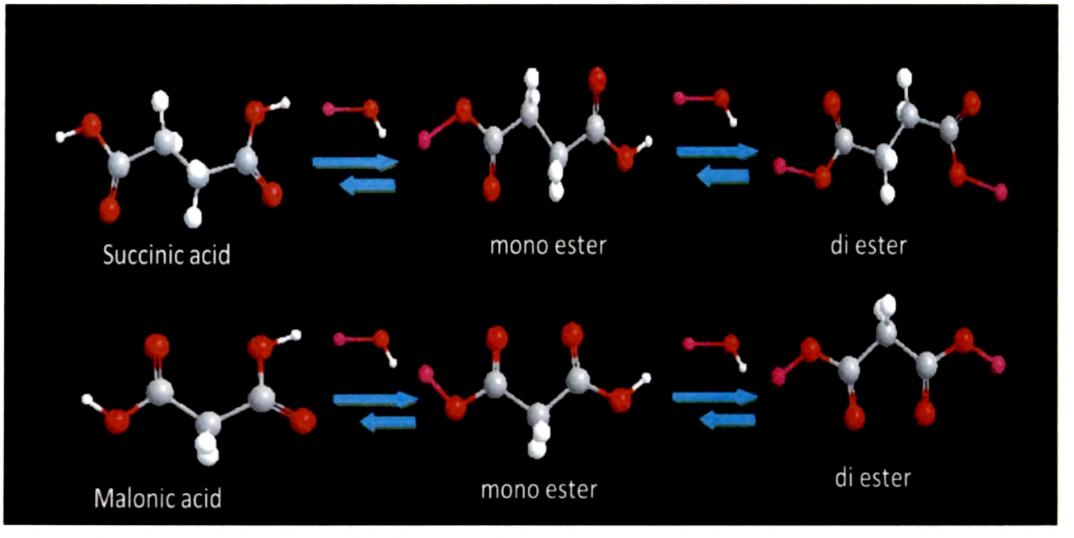

Figure 41. Esterification of succinic acid and malonic acid

The esterification reaction is an equilibrium-limited reaction. In order to overcome the equilibrium limitation, it is necessary either to carry out esterification by taking one of the reactant in excess. The yields can be increased by increasing the concentration of either alcohol or acid. In a practical means, to obtain maximum yield for economic reasons, the reactant that is usually less expensive is taken in excess. In present study corresponding alcohol is taken in excess.

Esterification of succinic acid and malonic acid with butanol

The effect of various reaction parameters such as % loading of TPA and TSA, acid/ alcohol molar ratio, amount of catalyst and reaction time were studied to optimize the conditions for maximum yields for diesters.

Effect of % loading of TPA/TSA

To study the effect of % loading the reaction was carried out with different catalyst containing different loading of TPA/TSA. The obtained results are shown in figure 42.

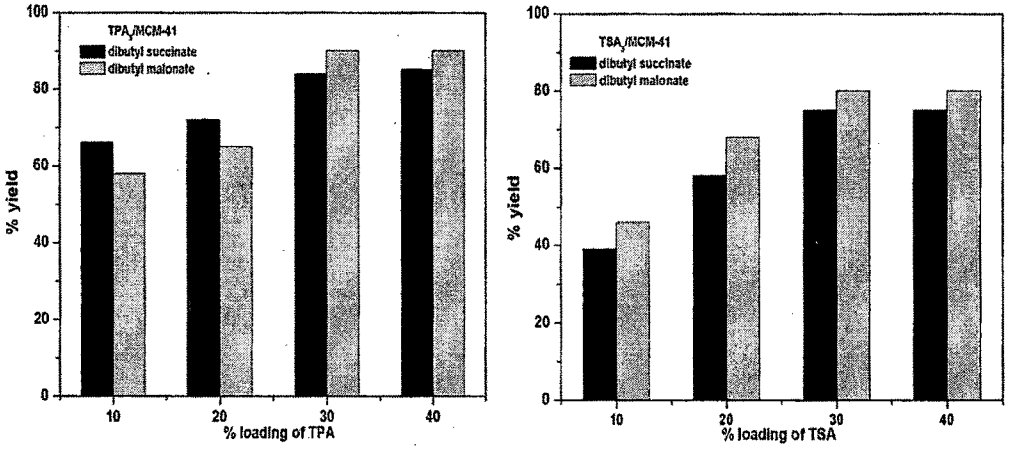

Figure 42. Effect of % loading of TPA/TSA; Reaction conditions: mole ratio of acid/ alcohol: 1:3,Amount of catalyst: 0.1 g, Reaction temperature 80 °C, Reaction time: 8 h for succinate esters, 4hrs for malonate estrers.

It is observed from the figure 42 that with increase in the % loading of TPA/ TSA, % yield towards diester also increases. For 30 and 40% loading, the difference in % yield is not that much appreciable. Hence the catalyst containing 30% loading of HPA (TPA/TSA) i.e. TPA_3/MCM-41 and TSA_3/MCM-41catalyst were selected for the detail study. Optimization of reaction parameters for esterification of succinic acid and malonic acid with butanol was carried out over TPA_3/MCM-41 and TSA_3/MCM-41.

Effect of mole ratio of acid /alcohol

It is seen from the figure 43 that, with change in mole ratio of acid to butanol, there is drastic change in the yields of products. Initially, the yield towards diester increases from 1:2 to 1:3 molar ratios. On further increasing the alcohol concentration equilibrium is attained and no further increase in % yield of diester was observed. Hence, 1:3 molar ratio of reactants i.e. acid/ alcohol was selected for the detail study.

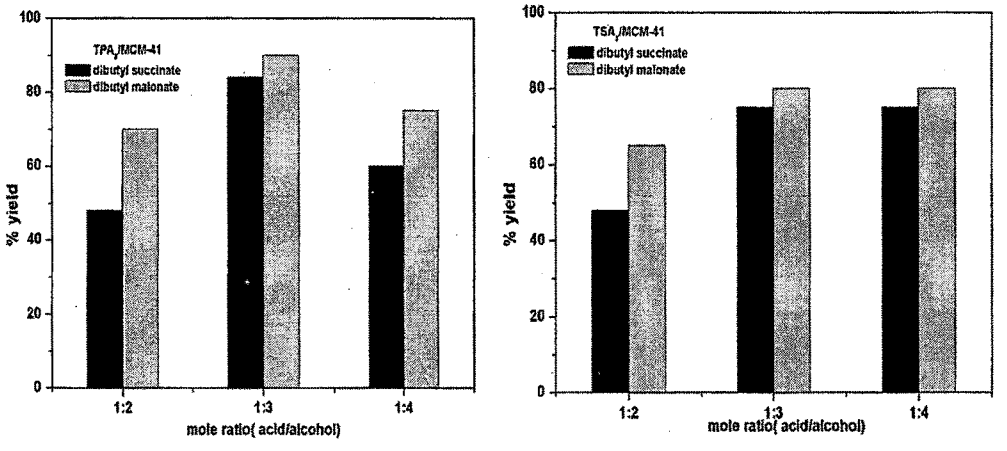

Figure 43. Effect of mole ratio of acid to alcohol; Reaction conditions: amount of catalyst 0.1 g, Reaction temperature 80°C, 8h for succinate esters, 4h for malonate estrers

Effect of amount of catalyst

To study the effect of the amount of the catalyst, the reaction was carried out with different amount of the catalyst keeping the mole ratio of acid to alcohol 1: 3 at 80 °C. As it is observed from figure 44 that with increase in amount of catalyst % yield towards diester increases. With 0.1 g of catalyst % yield towards diesters was maximum.

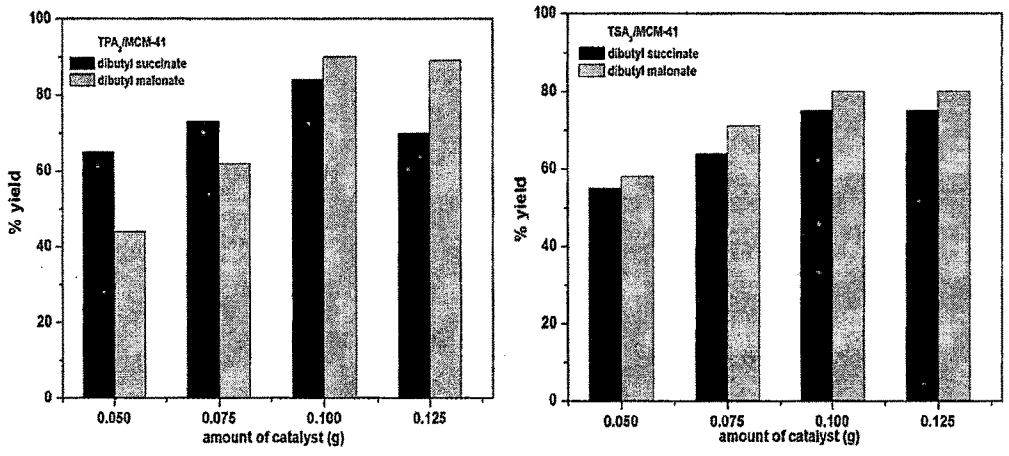

Figure 44. Effect of amount of catalyst; (Reaction conditions: Mole ratio of acid to alcohol; 1:3, Reaction temperature 80°C, Reaction time: 8h for succinate esters, 4hrs for malonate esters)

Effect of reaction time

Effect of reaction time was studied for esterification of succinic acid and malonic acid with butanol over TPA_3/MCM-41 and TSA_3/MCM-41. It was observed (figure 45) that the % yields of diester's increases with increase in reaction time.

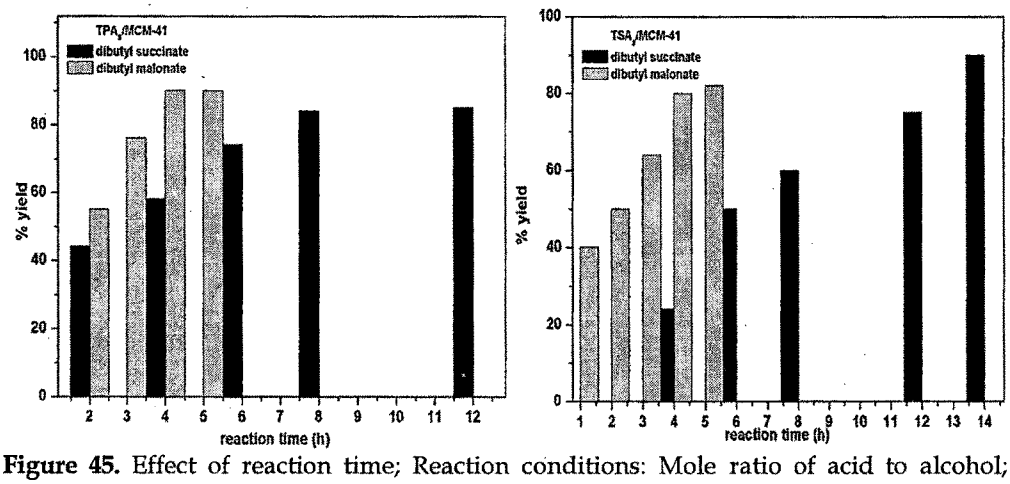

Figure 45. Effect of reaction time; Reaction conditions: Mole ratio of acid to alcohol; 1:3, amount of catalyst: 0.1g, Reaction temperature 80 °C .

The optimized conditions for esterification of succinic acid and malonic acid with n-butanol using TPA_3/MCM-41 are: Mole ratio of acid to alcohol 1:3; Amount of catalyst 0.1g; Reaction Temperature 80°C and Reaction Time 8h while for malonic acid reaction time was 4h.

The optimized conditions for esterification of succinic acid and malonic acid with n-butanol using TSA_3/MCM-41 are: Mole ratio of acid to alcohol 1:3; Amount of catalyst 0.1g; Reaction Temperature 80°C and Reaction Time 14h while for malonic acid reaction time was 4h.

The control experiments with support, MCM-41 and TPA/TSA were also carried out under optimized conditions

Table 15. Control experiments for esterification of dicarbixylic acid (succinic acid and malonic acid) with butanol

[a]Catalyst	%yield	
	dibutyl succinate	dibutyl malonate
[b]TPA	89[c]	94
[b]TSA	86[d]	85
MCM-41	<2	<5
TPA_3/MCM-41	85[c]	90
TSA_3/MCM-41	90[d]	80

[a]Reaction conditions: mole ratio alcohol to acid 1:3, amount of catalyst 0.1g, reaction temperature 80 °C, reaction time 4h for malonate esters; [b]amount of catalyst for TPA/TSA : 23mg ; [c]reaction time 12h; [d]reaction time 14h

It can be seen from Table 15 that support MCM-41 was not much active towards the esterification of succinic acid and malonic acid indicating the catalytic activity is mainly due to TPA/TSA. The same reaction was carried out by taking the active amount of TPA/TSA; 23 mg. It was found that the active catalyst TPA gives 89 and 94%, TSA 86 and 85% yield for dibutyl succinate and dibutyl malonate respectively. Almost the same activity was

obtained for the catalyst indicates that TPA/TSA is the real active species. Thus, we were successful in anchoring HPAs to mesoporous support MCM-41 without any significant loss in activity and hence in overcoming the traditional problems of homogeneous catalysis.

Esterification of dicarboxylic acids with different alcohols

The esterification of dicarboxylic acids (succinic acid/ malonic acid) with different alcohols such as ethanol, hexanol and octanol was also carried out under optimized conditions and the % yields of corresponding esters are shown in the figure 46.

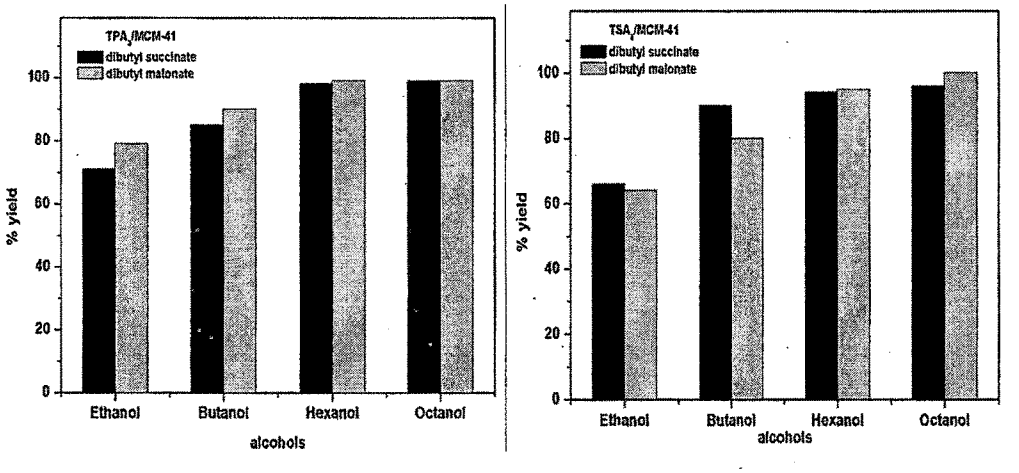

Figure 46. Esterification of dicarboxylic acid with different alcohols;Reaction conditions: Mole ratio of acid to alcohol; 1:3, Reaction temperature 80°C, Reaction time: 8 and 14h over TPA_3/MCM-41and TSA_3/MCM-41 respectively for succinate esters, 4hrs for malonate esters.

It is very interesting observation that formation of malonate esters is moreeasier than succinate esters over same catalyst. This may be due to the size of the reactants, malonic acid being C3 carbon molecule and succinic acid C4. Further malonic acid being smaller can easily diffuse in to the channels of the porous catalyst than Succinic acid being bigger facing considerable hindrance.

Regeneration and Recycling of the catalyst

Characterization of Regenerated Catalysts

In order to investigate the details of the deactivation, repeated use of the catalyst was examined. To see any change in the structure of catalyst after completion of reaction, the used catalysts were characterized for DRS, elemental analysis as well as acidity measurements.

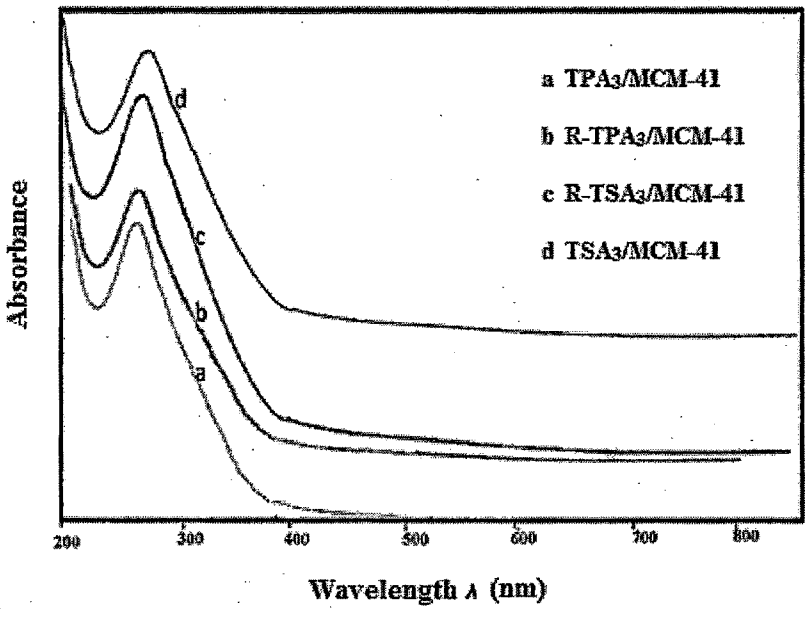

Figure 47. DRS of regenerated catalysts

Figure 47 illustrates the DRS of fresh catalyst as well as used catalysts. No difference in DRS indicates the stability of the used catalysts after the reaction. Further the filtrate of reaction mixture was also checked for the presence of any leached TPA /TSA by Uv-visible. The absence of blue colour indicates no leaching of TPA/TSA.

Leaching as well as Heterogeneity Test

Any leaching of the active species from the support makes the catalyst unattractive and hence it is necessary to study the stability as well as leaching of TPA/TSA from the support. Rigorous proof of heterogeneity can be obtained only by filtering the catalysts at the reaction temperature before completion of the reaction and testing the filtrate for activity [25].

The leaching of W from catalyst was confirmed by carrying out an analysis of the used catalyst (EDX) as well as the product mixtures (AAS). Analysis of the product mixtures shows that if any W was present it was below the detection limit, which corresponds to less than 1 ppm. These observations strongly suggest no leaching of any active species, TPA/TSA, form the support, MCM-41.

For the rigorous proof of heterogeneity, a test was carried out by filtering the catalysts from the reaction mixture at 80^0C after 4 h and the filtrate was allowed to react up to 6 h. The reaction mixture of 4 h and the filtrates were analyzed by Gas Chromatogram. From the heterogeneity test it was found that there was no change in the % yield of esters, indicating the present catalyst fall into category-C [25]. On the basis of these results, it can be concluded that there is no leaching of TPA or TSA species from the support MCM-41 in case of TPA_3/MCM-41 and TSA_3/MCM-41 catalysts respectively and the present catalysts are truly heterogeneous in nature.

Table 16. Elemental analysis (EDS) and acidity characterization of reused catalysts

Catalyst	Elemental analysis (weight %)						Total acidity (mmol/g)
	O	Si	W		P		
			By EDS	Theoretical	By EDS	Theoretical	
TPA_3/MCM-41	53.9	27.8	18.0	19	0.30	0.32	1.41
R-TPA3/MCM-41	53.9	27.9	17.8	19	0.30	0.32	1.40
TSA_3/MCM-41	53.92	28.12	17.97	19	-	-	1.33
R-TSA_3/MCM-41	54.2	27.9	17.8	19	-	-	1.30

The EDS analysis and the acidity of the fresh as well as the reused catalyst was carried out and the obtained results are shown in Table 16.The elemental analysis values of the recycled catalysts were close to that for fresh catalysts. Further the total acidity values of reused catalysts were almost the same as compared to the fresh catalysts. Hence there is no deactivation of catalyst. This also confirms the truly heterogeneous mode of action.

Catalytic activity of regenerated catalysts

The catalyst was recycled for four times in order to test its activity as well as stability. The catalyst was separated from the reaction mixture by simple filtration, washed with double distilled water till the filtrate was free from the unreacted succinic acid /malonic acid, if any, dried at 100 °C and the recovered catalysts were charged for the further run. The obtained results are as shown in figure 48. It is seen from the table that the catalysts can be used up to four cycles without any appreciable change in the percentage yield.

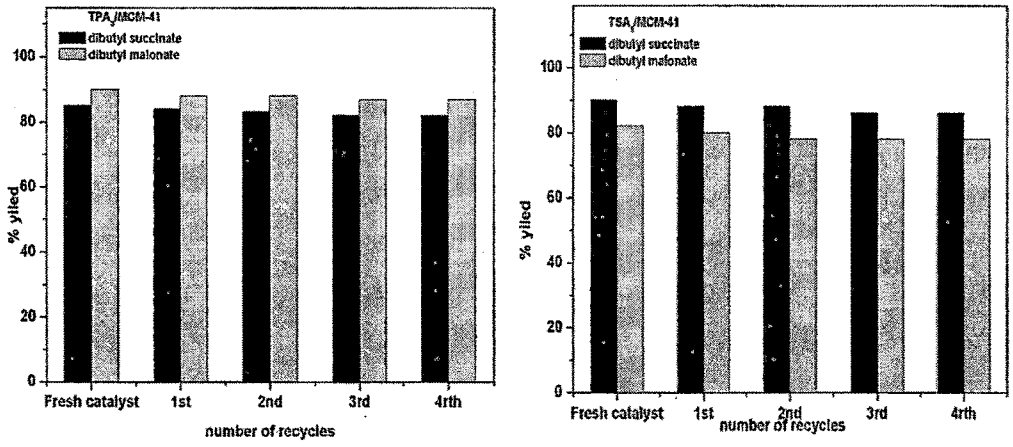

Figure 48. Recycling of the catalysts; Reaction conditions: Amount of catalyst: 0.1 g, mole ratio of acid/ alcohol: 1:3, Reaction time: 8 h and 14 h for succinate esters over TPA_3/MCM-41 and TSA_3/MCM-41 respectively, 4 h for malonate esters , Reaction temperature 80 °C

Comparison with reported catalyst

It is observed from the table 17 that much higher yields were obtained for dibutyl succinate with the reported catalyst [5, 7, 8] but the amount of catalyst required is very high i.e. 0.5 g, where as in the present case only 0.1 g is required. For diethyl succinate also considerably high yield were obtained as compared to the other reported catalysts [10, 12, 17].

Further the % yield for dibutyl malonate is comparatively low in case of reported catalysts [7, 17] where as in the present case it is 90%.The present catalysts are advantageous in three ways that is low amount of catalyst, short reaction time,and higher yields of dibutyl malonate. Thus, the superiority of the present catalyst lies in obtaining higher yields of diesters under mild reaction conditions.

Table 17. Comparison with reported catalysts

Reference	Catalyst	Alcohol	[a] Reaction conditions	% Yield dialkylsuccinate	% Yield dialkylmalonate
Present work	**TPA_3/MCM-41**	**Butanol**	**0.1:3:80:8**	**85**	**90 [b]**
Present work	**TPA_3/MCM-41**	**Ethanol**	**0.1:3:80:8**	**71**	**79[b]**
Present work	**TSA_3/MCM-41**	**Butanol**	**0.1:3:80:14**	**90**	**80[b]**
Present work	**TSA_3/MCM-41**	**Ethanol**	**0.1:3:80:14**	**66**	**64[b]**
[5]	Al^{+3} -mon	Butanol	0.5:3:80:8	94	77
[8]	IB	Butanol	0.2:5:80:8	94	-
[7]	Al^{+3} -mon	Iso-butanol	0.5:3:80:8	96	24
[10]	Starbon-400-HSO_3	Ethanol	0.1:30:80:8	95	-
[10]	DARCO-HSO_3	Ethanol	0.1:30:80:8	27	-
[12]	PW/Al-MCM-41	Ethanol	0.1:3:120:12	11	-
[17]	ZTPA(zirconium titanium phosphate)	Ethanol	0.2:2.5:145:10	-	79

a: reaction conditions: amount of catalyst (%w/w, in some cases unit is gm):mole ratio of alcohol/ acid: reaction temperature: reaction time(h); [b]reaction time for malonic acid esterification 4 h

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(b)Esterification of long chain fatty acids with alcohols

The esterification of fatty acid with short chain alcohols is very important due to their industrial applications. The fatty acid esters constitute an important class of useful chemical intermediates in the synthesis of several products such as amides, sulfonates and fatty alcohols. These compounds can be used as solvents, spreading or softening agents in polymers. They are also used in the textile, cosmetic and rubber industries [1]. For example, esters produced from long-chain fatty acids (12–20 carbon atoms) as well as short-chain fatty acids (2–8 carbon atoms) are used increasingly in the food, detergent, and plasticizer, and lubricant, cosmetic and pharmaceutical industries [2].

Traditionally the fatty acid esters are produced in batch reactors using strong acids like sulphuric acid [3, 4]. These processes suffer from high cost separation procedures, large energy consumption and the production of polluting by-products. As these reactions are equilibrium limited, high conversions can be only obtained by using a large excess of alcohol which is again not desired due to the economic reasons. A number of reports are available on the esterification reactions of fatty acids using various heterogeneous catalysts [5-15].

M. da Silva-Machado et al reported esterification of lauric acid with glycerol using modified zeolite beta catalyst. The influence of different catalyst parameters on the activity and selectivity of the reaction were discussed but there was no data about catalyst recycling [6].

Y. Sugi and co-workers reported aluminium and zirconium containing mesoporous materials esterification of lauric acid with glycerol in supercritical CO_2 medium [7].

Sang-Wook Park and co-workers reported esterification of lauric acid with isopropyl alcohol by tricaprylmethylammonium chloride as a catalyst. They also reported several kinds of reaction rate constant, from which equilibrium constants were expressed as a function of reaction temperature. The found that the reaction was between a very slow and slow reaction regime [9].

M.C. de Jong's group reported the reaction kinetics of the esterification of myristic acid with iso-propanol with n-propanol, using p-toluene sulphonic acid (p-TSA) as catalyst, for a temperature range of 343–403 K. The reactions follow first order kinetics in all components [10]. X. Hu et al have reported esterification of different fatty acids with Sulfated zirconia catalysts. They have correlated the catalytic activity with number of carbon atoms and degree of unsaturation in fatty acid. The longer the carbon chain is, the more difficult it is to react; the higher the unsaturation level is, the more difficult it is to respond [15].

V. K. Gupta and co-workers have reported silica-supported sulfuric acid catalyst for esterification of myristic acid with isopropyl alcohol. The recycled catalyst showed low activity due to a reduction of acid sites in the recycled catalyst due to the acid leaching [14]. S. Bhatia and group reported kinetic data on the esterification of palmitic acid with isopropanol using homogeneous (para-toluene sulfonic acid, p-TSA) and heterogeneous (zinc ethanoate coated on silica gel, ZnA/SG) catalysts in a batch reactor. They reported second order kinetics for the same with much lower activation energy than the traditional catalysts. They have not described about the catalysts regeneration and recycling [16].

M. A. Yarmo' group has reported 12-Tungstophosphoric acid supported on MCM-41 for esterification of fatty acid at 120 ^{0}C [17]. The same group has also

reported another catalyst zirconium sulfate ($Zr(SO_4)_2 \cdot 4H_2O$) for the esterification of different fatty acids with butanol [18].

A literature survey shows that the esterification of lauric acid with glycerol was carried out over number of solid acid catalyst. A literature survey shows that there are very few reports available for esterification of lauric acid with primary alcohols. Therefore, it was thought of interest to carry out esterification of lauric acid with butanol. Further a detail study on kinetic behaviour was also carried out.

The present chapter describes esterification of lauric acid with butanol over TPA/TSA anchored to MCM-41. The effect of various reaction parameters such as catalyst concentration, acid/ alcohol molar ratio and temperature were studied to optimize the conditions for maximum conversion. Also the catalyst was regenerated and reused. The kinetics of the reaction was also studied. The rate of reaction and order of reaction was determined. The effect of temperature on rate constant was studied, and the activation energy was calculated by fitting the results in to Arrhenius equation. Based on the catalytic and kinetic data the best catalyst was also proposed.

Experimental

Materials

All chemicals used were of A.R. grade. Lauric acid and n-butanol were used as received from Merck.

Catalytic reaction

The esterification of lauric acid with alcohols were carried out in a 50ml batch reactor provided with a double walled air condenser, Dean-Stark apparatus, magnetic stirrer and a guard tube. Dean-Stark apparatus was attached to a round bottom flask to separate the water formed during the reaction. The reaction mixture was refluxed at 90°C for 4 h. The obtained products were analyzed on a Gas Chromatograph (Nucon-5700) using BP1 capillary column. Products were identified by comparison with the authentic samples and finally by Gas Chromatography-Mass Spectroscopy (GC-MS). Turnover number (TON) is defined as mole substrate reacted per mole of the catalyst, and was calculated using following formula:

$$\text{TON} = \left(\frac{\text{number of moles of substrate reacted}}{\text{number of moles of catalyst}} \right)$$

The turnover number per unit time is called TOF.

RESULTS AND DISCUSSION

Esterification of Lauric acid with n-butanol

The esterification of fatty acid is an equilibrium-limited reaction. In order to overcome the equilibrium limitation, generally esterification of fatty acids is carried out by taking alcohol in excess in order to favor the forward reaction. In the present case butanol was taken in excess for economic reasons. The esterification of lauric acid with alcohol is shown in figure 49.

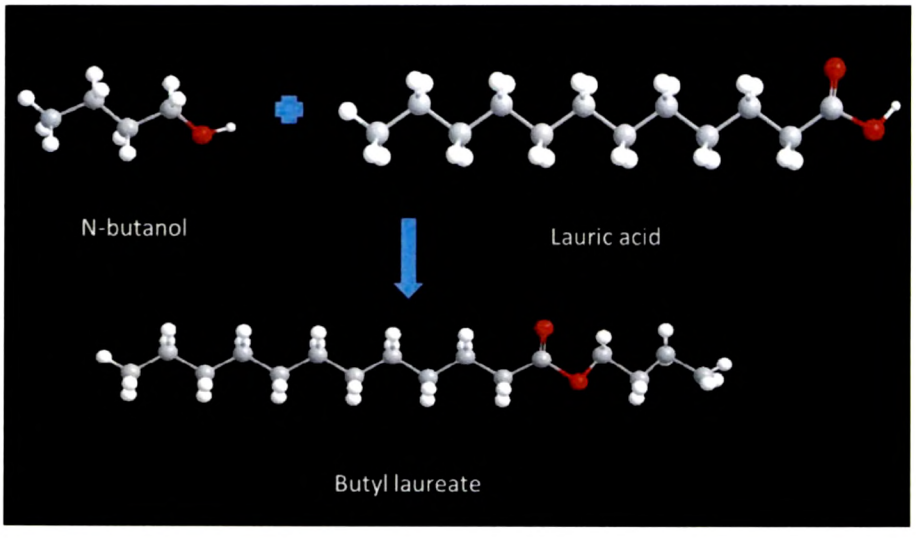

Figure 49. Esterification of lauric acid with alcohol.

The effect of various reaction parameters such as % loading of TPA and TSA, acid/ alcohol molar ratio, amount of catalyst and reaction time were studied to optimize the conditions for maximum conversion of lauric acid.

Effect of % loading of TPA/TSA

The esterification reaction was carried out with 10, 20, 30 and 40% loadings of TPA/TSA. The obtained results are shown in Figure 50. It is observed from the figure that with increase in the % loading of TPA/TSA conversion also increases. For 10% and 20% loadings of TPA, conversion of lauric acid was considerably low in case of TPA_3/MCM-41. For 30 and 40% loading, the difference in % conversion is not that much appreciable. Hence the catalysts containing 30% loading of TPA/TSA i.e. TPA_3/MCM-41 and TSA_3/MCM-41 catalysts were used for the detail study.

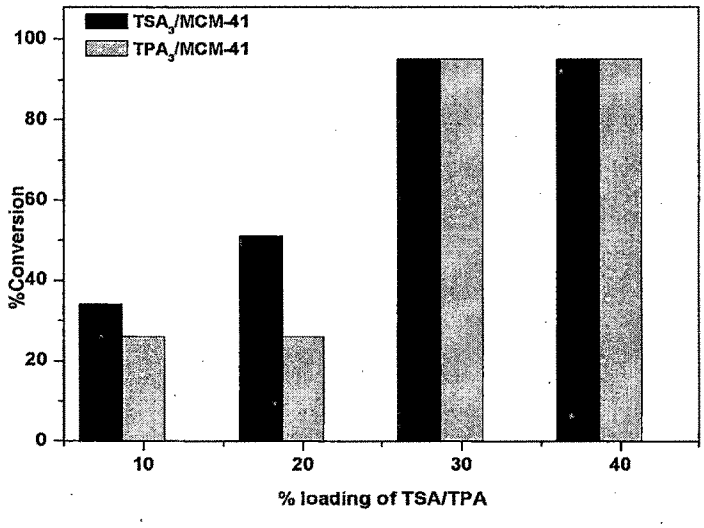

Figure 50. Effect of % loading of TPA/TS; (reaction conditions: mole ratio of acid to alcohol 1:2, amount of catalyst 0.2 g, reaction temperature 90 °C, reaction time 3 and 4 h for TPA/MCM-41 and TSA/MCM-41 respectively)

Effect of Mole ratio of acid/alcohol

The reaction was carried out by varying mole ratio of lauric acid to n-butanol with 0.2 g of the catalyst. It is observed that with increase in concentration of alcohol the % conversion of lauric acid increases (figure 51). With 1: 2 mole ratio of lauric acid to n-butanol, maximum conversions were achieved with all the catalysts. With further increase in n-butanol concentration not much difference was observed. Hence, further reactions were carried out in 1:2 molar ratio of acid to alcohol.

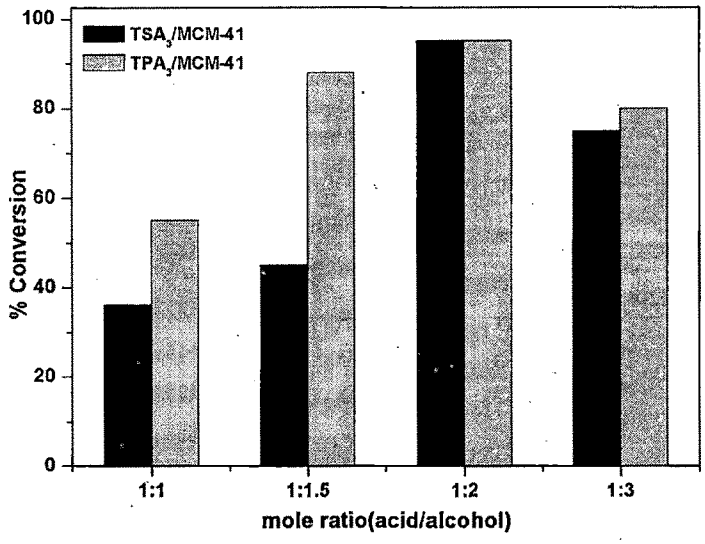

Figure 51. Effect of Mole ratio of acid/alcohol; (Reaction conditions; amount of catalyst 0.2 g, reaction temperature 90 °C, reaction time 3 h and 4 h for TPA/MCM-41 and TSA/MCM-41 respectively)

Effect of amount of catalyst

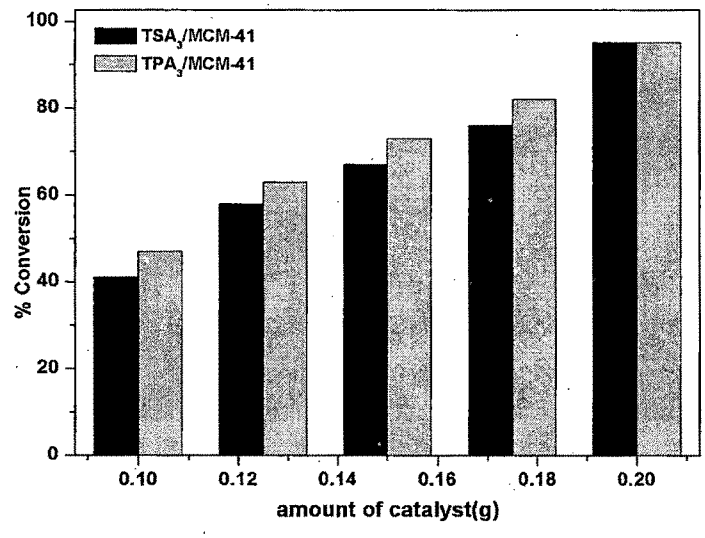

Figure 52. Effect of amount of catalyst; (Reaction conditions; acid to alcohol Mole ratio of acid /alcohol 1:2, reaction temperature 90 °C, reaction time 3 h and 4 h for TPA/MCM-41 and TSA/MCM-41 respectively)

To study the effect of the amount of the catalyst, the reaction was carried out with different amount of the catalyst keeping the mole ratio of acid to alcohol 1:2 for 4 h at 90 °C.

Effect of amount of catalyst on lauric acid conversion was investigated. The catalyst amount was varied in the range of 0.1-0.2g. As shown in Figure 52, the lauric acid conversion increases with the increase in catalytic amount of TPA_3/MCM-41 or TSA_3/MCM-41 and reaches to a maximum conversion. But with further increase in amount of catalyst the lauric acid conversion remains constant and no further increase in the % conversion with increase in amount of catalyst indicates the attainment of the maximum equilibrium. The obtained results are as expected. Hence, 0.2 g is the optimized amount of the catalyst.

Effect of reaction time

With increase in reaction time conversions of lauric acid increases (figure 53) up to three hours maximum 95% conversion of lauric acid was achieved over TPA_3/MCM-41. Further it does not increase with time. In case of TSA_3/MCM-41 maximum conversion was achieved in four hours.

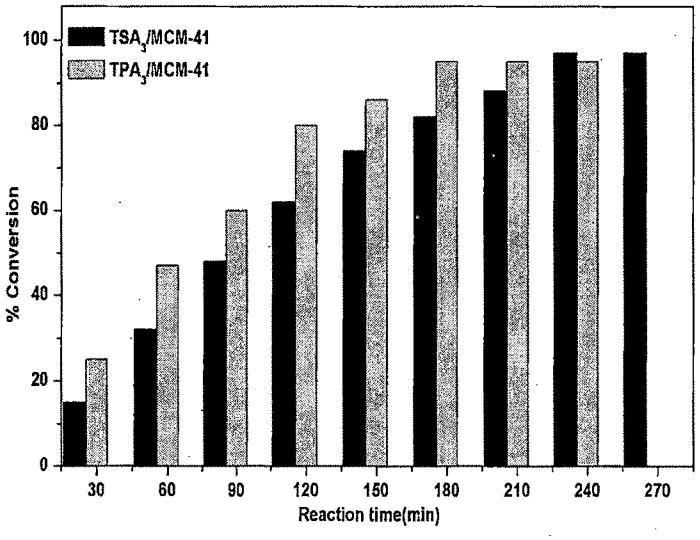

Figure 13. Effect of reaction time; (Reaction conditions; amount of catalyst 0.2g, acid to alcohol mole ratio 1:2, reaction temperature 90 °C)

Effect of reaction temperature

With increase in reaction temperature the conversion of lauric acid increases (figure 54). At 90 ^{0}C maximum conversion was obtained.

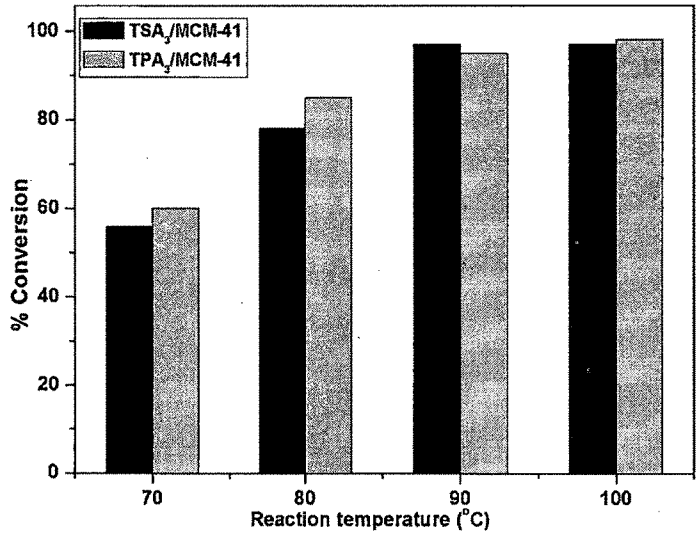

Figure 54. Effect of reaction temperature; (reaction conditions: mole ratio of acid to alcohol 1:2, amount of catalyst 0.2 g, reaction time 3 and 4 h for TPA/MCM-41 and TSA/MCM-41 respectively)

The optimized conditions for esterification of lauric acid are: Mole ratio of acid to alcohol 1:2; Amount of catalyst 0.2 g; Reaction Temperature 90 ^{0}C. Reaction time was 3 h and 4 h for TPA_3/MCM-41 and TSA_3/MCM-41 respectively.

The control experiments with support, MCM-41 and TPA/TSA were also carried out under optimized conditions

Table 18. Control Experiments for esterification of lauric acid

[a]Catalyst	% Conversion
[b]TPA	92
[b]TSA	90
MCM-41	<2
TPA_3/MCM-41	97
TSA_3/MCM-41	95

[a]Reaction conditions: acid to alcohol Mole ratio of acid /alcohol 1:2, reaction temperature 90 °C, reaction time 3 h and 4 h for TPA/MCM-41 and TSA/MCM-41 respectively; [b]amount of catalyst for TPA/TSA : 46 mg

It can be seen from table 18 that support MCM-41 was not much active towards the esterification of lauric acid indicating the catalytic activity is mainly due to TPA/TSA. The same reaction was carried out by taking the active amount of TPA/TSA; 46 mg. It was found that the active catalysts, TPA and TSA gives 92 and 90% conversion respectively. Almost the same activity was obtained for the catalysts indicates that TPA/TSA is the real active species. Thus, we were successful in anchoring HPAs to mesoporous support, MCM-41 without any significant loss in activity and hence in overcoming the traditional problems of homogeneous catalysis.

Regeneration and Recycling of the catalyst

Characterization of Regenerated catalysts

The regenerated catalysts were characterized for DRS, elemental analysis (EDS), acidity measurements, leaching as well as heterogeneity test, in order to confirm the retention of the catalyst structure, after the completion of the reaction as discussed earlier. The results are same and hence are not included.

Catalytic activity of regenerated catalysts

The catalysts were recycled in order to test its activity as well as stability. The catalyst was separated from the reaction mixture only by simple filtration, washed with conductivity water till the filtrate is free from the acid dried at 100^{0}C and the recovered catalyst was charged for the further run. There is no appreciable change in the %conversion using regenerated catalysts up to four cycles (figure 55).

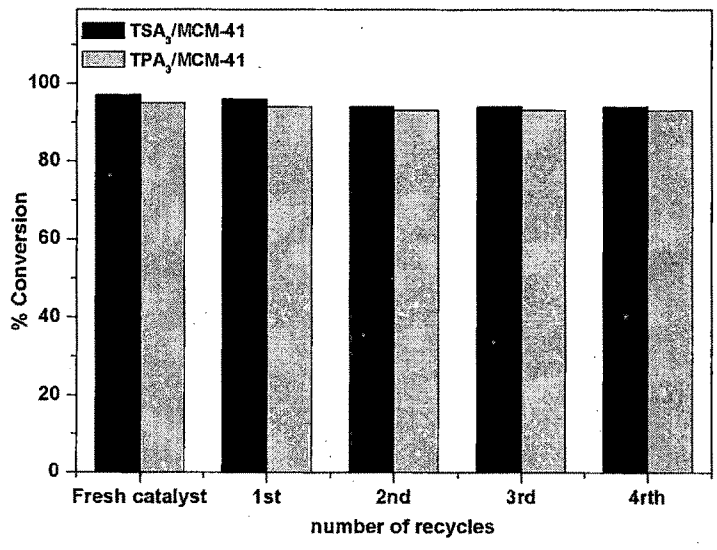

Figure 55. Recycling of catalyst; (Reaction conditions; amount of catalyst 0.2 g, acid to alcohol mole ratio 1:2, reaction temperature 90 °C, reaction time 3 h and 4 h for TPA/MCM-41 and TSA/MCM-41 respectively)

Comparison of the different catalysts for esterification of lauric acid and Butanol

The superiority of the present catalyst lies in obtaining higher conversions of lauric acid under mild reaction conditions. It is observed from the Table 19 that 93% conversion was obtained using sulphuric acid catalyst [17], although mole ratio and reaction time has been minimized but high reaction temperature and drawbacks of homogeneous sulphuric acid catalyst are well known.

Table 19. Comparison of the different catalysts for esterification of lauric acid and butanol

Reference	Catalyst	[a]Reaction conditions	%conversion	TOF (min^{-1})
Present work	TPA_3/MCM-41	0.2g;1:2;90;3	98	19.45
Present work	TPA_3/MCM-41	0.2g;1:2;90;4	95	25.93
[17]	sulfuric acid (H_2SO_4)	5wt%;1:1.2;120;4	93	0.04
	para-toluene sulfonic acid (PTSA)	5wt%;1:1.2;120;4	87	0.07
	bulk heteropoly acids (TSA)	5wt%;1:1.2;120;4	88	0.30
	bulk heteropoly acids (TPA)	5wt%;1:1.2;120;4	81	0.89
[18]	Zirconium sulfate ($Zr(SO_4)_2$ $4H_2O$)	5wt%;1:1.2;120;4	88.2	-
[15]	Sulfated zirconia (SO_4/ZrO_2)	2g;1:8;120;6	99.5	-

[a]Reaction conditions: amount of catalyst wt%; mole ration oleic acid to alcohol; reaction temperature °C; reaction time h

Unsupported 12-tungstophosphoric acid and 12-tungstosilcic acid [17] shows considerably high TOF values as compared to sulfuric acid but the disadvantages of conventional homogeneous catalysts are well known. In case of suphated zirconia [15] catalyst 99.5% conversion was achieved in 6 hours but there was no data about catalyst regeneration and recycling. Zirconium sulfate ($Zr(SO_4)_2 .4H_2O$) catalyst[18] shows 88 % conversion , but after first recycle itself it shows 15% of loss in the conversion.

The present catalyst exhibits high conversion as well as TOF values as compared to the different catalysts reported in the literature under mild reaction conditions. In the present case TOF order is TPA_3/MCM-41 >TSA_3/MCM-41.

Kinetics

A detail study on kinetic behavior for esterification of lauric acid with 1-butanol was carried out over TPA_3/MCM-4 and TSA_3/MCM-4. In all the experiments, reaction mixtures were analyzed at fixed intervals at fixed intervals of time using gas chromatography.

Determination of rate constant and order of reaction.

For the irreversible bimolecular-type second order reaction

$$A+B \xrightarrow{\text{Catalyst}} \text{Product} \qquad \text{----------[1]}$$

The rate of consumption of A, ($-r_A$) is given by

$$r_A = k[C][A][B] \qquad \text{----------[2]}$$

The concentration of catalyst is constant throughout the reaction. Therefore,

$$r_A = k'[A][B] \qquad \text{---------- [3]}$$

Where $k'=k\,[C]$, [A] = Concentration of fatty acid, Lauric acid.

[B] = Concentration of alcohol, 1-butanol.

The integrated form of equation [3] is

$$\ln [a(b-x)/b(a-x)]=(b-a)\,k'\,t \qquad \text{----------[4]}$$

where x= Fraction of the product formed

a= Initial concentration of fatty acid (mmol/ml)

b= Initial concentration of alcohol (mmol/ml)

k'= second order rate constant

The figure 56 shows second order plot for esterification of lauric acid with butanol. The linearity of the data indicates that esterification of lauric acid follows second order rate law.

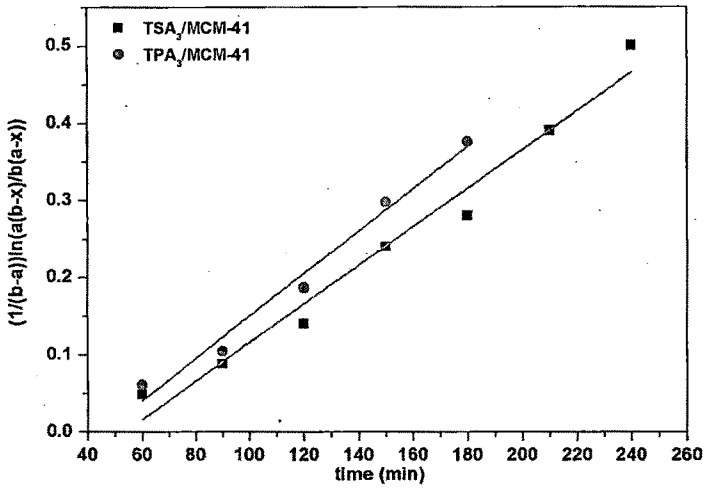

Figure 56. Second order plot for esterification of lauric acid with butanol

Effect of catalyst concentration on rate of reaction was also studied (figure 57). The increase in catalyst concentration shows noticeable effect on conversion of lauric acid. This can be attributed to higher number of substrate molecules get activated in presence of catalyst. Thus the nucleophilic attack by 1-butanol becomes more favorable and consequently, an increase in the formation of ester was observed. Hence with increase in catalyst concentration rate of reaction also increases.

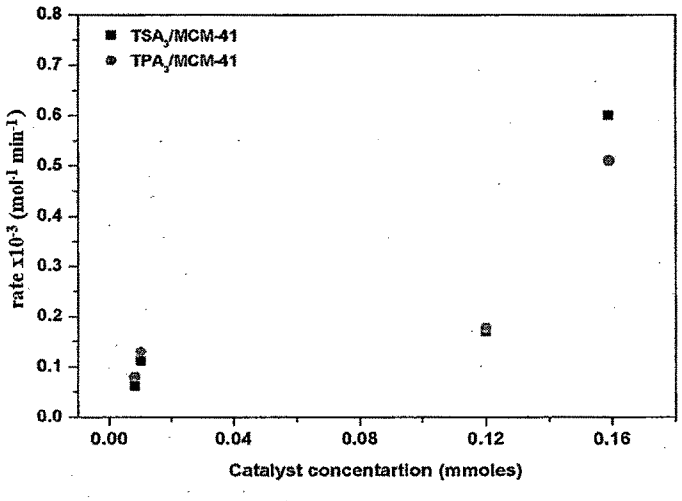

Figure 57. Plot of reaction rate vs catalyst concentration

Determination of Activation Energy

It was verified that temperature affects both reaction rate and conversions. With increase in temperature high conversions were achieved. The increase in reaction temperature caused corresponding increase in the reaction rate, especially in the range of 343-373 K. From this data Arrhenius plot was constructed and from the obtained curve pre-exponential factor (A) and activation energy (Ea) for this reaction was calculated (figure 58).

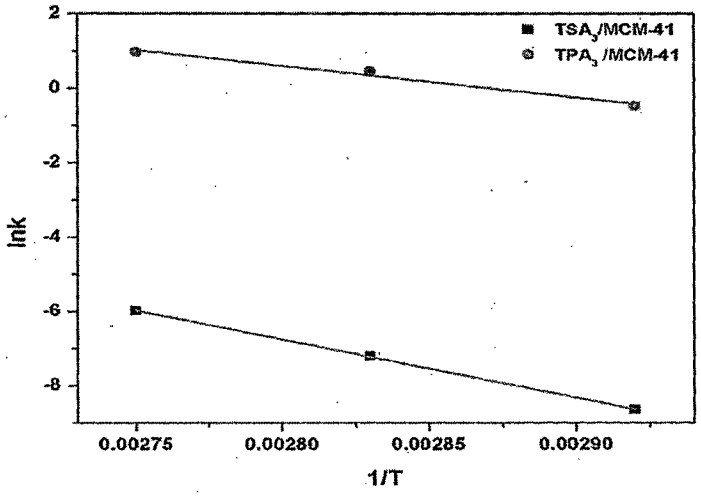

Figure 58. Arrhenius plot for esterification of lauric acid with n-butanol.

The kinetic parameters such as rate of reaction, pre- exponential factor (A) and activation energy (Ea) were calculated for all the catalysts and are presented in table 20. TPA_3/MCM-41 shows lower activation energy than TSA_3/MCM-41 due to the type of heteropolyanion. The effect of heteropolyanion will be discussed in detail later.

Table 10. Kinetic parameters for esterification of lauric acid with butanol

Catalyst	Kinetic parameters		
	Rate of reaction ($mol^{-1}min^{-1}$)	Arrehenius constant(A) ($mol^{-1}min^{-1}$)	Activation energy(Ea) ($kJmol^{-1}$)
[a]TPA_3/MCM-41	$2.3x10^{-3}$	27	78
[b]TSA_3/MCM-41	$1.35x10^{-3}$	37	130

Reaction conditions: Amount of catalyst: 0.1 g, mole ratio: 1:2, reaction temperature: 90 ^0C, [a]reaction time: 3 h. [b] reaction time 4 h

It is important to observe that whether the reaction rate is diffusion limited/mass transfer limited or it is truly governed by the chemical step where the catalyst is being used to its maximum capacity. It is reported that the activation energy for diffusion limited reactions is as low as 10-15 $kJmol^{-1}$ and for reactions whose rate is governed by a truly chemical step usually show activation energy excess of 25 $kJmol^{-1}$[19].In the present case the observed activation energy for both the catalysts was found to be greater than 25 $kJmol^{-1}$ (table 20) indicating rate is truly governed by chemical step.

Effect of heteropolyanion (Effect of heteroatom)

The catalytic activity of heteropoly acids TPA and TSA anchored to MCM-41 was compared in different reactions to see the effect of heteropolacid. Table 21 shows the catalytic activity of TPA_3/MCM-41 and TSA_3/MCM-41 in estreification of dicarboxylic acids, succinic acid and malonic acid. Higher yields of diesters, dibutyl succinate and dibutyl malonate, indicates the superior activity of TPA_3/MCM-41

Table 21. Esterification of dicarboxylic acids

Catalyst	Alcohol	% Yield	
		dialkylsuccinate	dialkylmalonate[b]
TPA_3/MCM-41	Butanol	85	90
TPA_3/MCM-41	Ethanol	71	79
TSA_3/MCM-41	Butanol	60	80
TSA_3/MCM-41	Ethanol	37	45

[a]Reaction conditions: amount of catalyst 0.1g: mole ratio of alcohol/acid 1:3; reaction temperature 80^{0}C; reaction time 8 and 4h for dialkylsuccinate and dialkylmalonate

The comparison of catalytic activity of TPA_3/MCM-41 and TSA_3/MCM-41 in esterification of lauric acid with butanol is shown in Table 22. It can be observed from Table 22 that the value of activation energy for TPA_3/MCM-41 is less than that of TSA_3/MCM-41 indicating the former is more active. This difference in catalytic activity is due to the nature of heteropoly acid. It is well known that TPA is more acidic as compared to that of TSA and hence the results are as expected. The high surface area, total acidity as well as higher TOF value observed for TPA_3/MCM-41 all adamantly reveal the superior activity of TPA_3/MCM-41 as compared to TSA_3/MCM-41.

Table 22. Esterification of lauric acid with butanol

[a]Catalyst	Surface area (m^2/g)	Pore diameter (Å)	Total acidity (mmol/g)	Keggin ion density (HPA) nm^{-2}	Activation energy (kJ mol^{-1})	TOF (min^{-1})
TPA_3/MCM-41	360	30.13	1.44	0 .1741	78	25.93
TSA_3/MCM-41	349.26	29.23	1.33	0.1797	130	19.45

[a]Reaction conditions: mole ratio of acid to alcohol 1:2, amount of catalyst 0.2 g, reaction temperature 90°C, reaction time 3 and 4h for TPA_3/MCM-41 and TSA_3/MCM-41 respectively.

The acid strength of heteropolyacids, follows the following order TPA>TSA. TPA_3/MCM-41 shows superior activity as compared to TSA_3/MCM-41, as expected.

Effect of Support pore diameter (Pore Expanded MCM-41)

To study the effect of support pore diameter MCM-41 was synthesized with two different pore sizes i.e 4.7 and 5nm and were used anchoring TPA. Textural properties and the total acidity values of both the supports and catalysts are presented in the Table 23.

Table 23. Textural properties and total acidity.

Catalysts	Surface area (m^2/g)	Pore diameter (nm)	Total acidity (mmol/g)
MCM-41	659	4.7	0.79
TPA_3/MCM-41	360	3.0	1.44
PE-MCM-41	1317	5.0	1.1
TPA_3/PE-MCM-41	631	4.8	1.46

The comparison of catalytic activity of TPA_3/MCM-41 and TPA_3/PE-MCM-41 in esterification of succinic acid, malonic acid and lauric acid with butanol is shown in Table 24.

Table 24. Esterification of dicarboxylic acids and fatty acid

Catalyst	% Yield		% Conversion
	[a]dialkylsuccinate	[a]dialkylmalonate	[b]Lauric acid
TPA_3/MCM-41	74	78	62
TPA_3/PE-MCM-41	92	95	96

[a]Reaction conditions: Mole ratio of acid to alcohol; 1:3, Reaction temperature 80 °C, Reaction time: 6 and 4h for dibutylsuccinate and dibutylmalonate respectively. [b]Reaction conditions: mole ratio of acid to alcohol 1:2, amount of catalyst 0.2 g, reaction temperature 90 °C, reaction time 2h

It can be observed from Table 24 that higher catalytic activity was observed for TPA_3/PE-MCM-41 than that of TPA_3/MCM-41 indicating the former is more active. The obtained difference in catalytic activity may be due to the support textural properties, in particular the support pore diameter and this can be explained as follows.

The pore diameter of TPA_3/MCM-41 and TPA_3/PE-MCM-41 is 3 nm and 4.8 nm respectively. This difference in the pore diameters of the catalysts is due to their respective support. The large pore diameter of TPA_3/PE-MCM-41 facilitates the diffusion of reactants and products as compared to TPA_3/MCM-41.

Conclusion

- The catalytic activity of TPA_3/MCM-41 and TSA_3/MCM-41 was explored for esterification of dicarboxylic acids, succinic acid, and malonic acid.
- The catalysts show high activity in terms of higher yields toward diesters, especially for dioctylmalonate; 99% yield was obtained over TPA_3/MCM-41.
- We could successfully develop, a green process for synthesis of diesters over present catalysts (Figure 59)

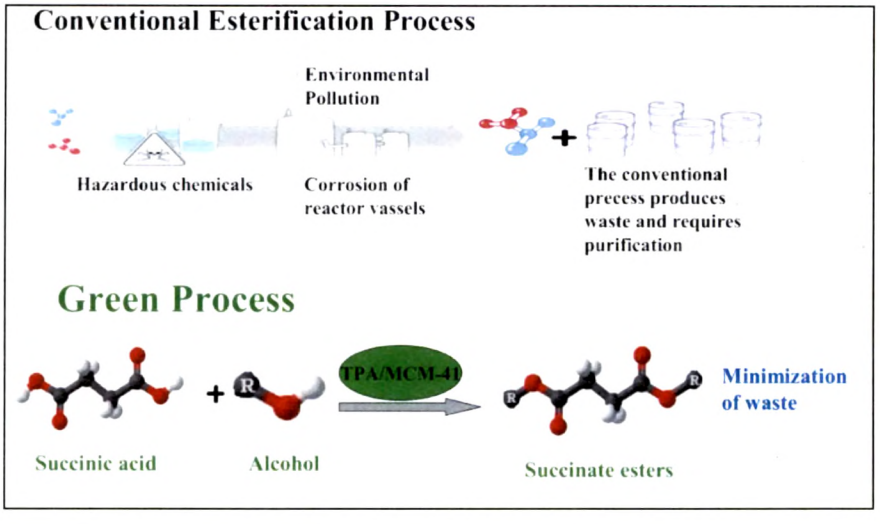

Figure 59. Green process for synthesis of diesters

- Esterification of fatty acid, lauric acid with 1-butanol was successfully carried out over TPA_3/MCM-41 and TSA_3/MCM-41.
- 97 and 95% conversion was obtained for lauric acid esterification over TPA_3/MCM-41 and TSA_3/MCM-41 respectively.
- The kinetic studies reveal that the reaction follows the second order kinetic law with respect to reactants as well as the catalyst.

- The influence of temperature on rate constant was also studied and the activation energy was found to be 78 and 130 $kJmol^{-1}$ with TPA_3/MCM-41 and TSA_3/MCM-41 respectively.
- The catalysts were regenerated and reused successfully up to four cycles.
- EDS, DRS as well as acidity studies of reused catalysts shows no structural changes indicating catalytic systems are stable.
- The TPA_3/MCM-41 shows superior catalytic activity as compared to TSA_3/MCM-41.
- TPA_3/PE-MCM-41 exhibits excellent catalytic activity as compared to TPA_3/MCM-41 due higher pore diameter of former than the later.
- Also the catalytic results demonstrated that the size of the support channels plays a crucial role in catalyst performance

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